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(54) Thickener for electrode paste and electrode paste composition for alkaline storage battery

(57) The present invention relates to a thickener for electrode paste for an alkaline storage battery comprising a water-insoluble water-absorbent resin; a composition for an electrode paste comprising an active material, a conductive agent, a fluorine resin and a thickener, wherein the thickener comprises a water-insoluble water-absorbent resin; and an electrode paste for an alkaline storage battery produced by adding water to the composition for the electrode paste.

The present invention provides electrode paste for an alkaline storage battery which allows thickening in a short time without forming undissolved powder lumps in the process of thickening by adding water, uniform application without sedimentation of active material or conductive agent even when used in a small amount, good applicability without sagging after application, and without liability of elution in electrolyte.

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Description

The present invention relates to a thickener used as a component in the production of an electrode paste as the positive electrode, such as nickel positive electrode, or the negative electrode, such as cadmium negative electrode and hydrogen-storing alloy negative electrode, in alkaline storage batteries such as nickel-cadmium and nickel-hydrogen batteries; and to a composition for preparing an electrode paste and an electrode paste using the thickener.

Conventional electrodes in alkaline storage batteries are classified into two kinds, namely sintered type and non-sintered type (paste type), according to the production process. Recently, the paste type electrodes are more commonly used owing to their easier production process. A paste type nickel positive electrode is commonly produced by mixing an active material such as powder of nickel hydroxide, and a conductive agent such as carbon black, nickel and cobalt metal powders; adding a fluorine resin thereto so as to firmly bond the active material; further adding an aqueous solution of a thickener to produce a paste; applying the paste to a metal porous substrate; drying the substrate, and pressure molding. Examples of conventional thickeners include water-soluble polymers such as carboxymethyl cellulose (CMC), polyvinyl alcohol and sodium polyacrylate. A paste type negative electrode is often produced similarly, except that active materials for a negative electrode such as cadmium powders and hydrogen-storing alloy powders are used, by preparing a paste of an active material, a conductive agent, a fluorine resin and an aqueous solution of a thickener, then applying the paste to a metal porous substrate, drying the substrate, and pressure molding.

However, the following problems ① to ③ have been encountered when a water-soluble polymer is used as the thickener in the production of an electrode paste.

① Since the active material or the conductive agent in the paste tends to sediment, uniform application of the paste to the metal porous substrate is difficult; in addition, the paste once applied to the metal porous substrate tends to sag. Moreover, if the amount of the water-soluble polymer is increased to prevent the sedimentation or sagging, since the stringiness is intensified to deteriorate the applicability to the metal porous substrate as well as to diminish the activity by covering the surface of the active material with the thickener, a deleterious effect on battery characteristics results. "Stringiness" herein denotes a phenomenon in applying a paste to a substrate, namely roping of the paste between the substrate and the coating appliance at the time of removing the coating appliance from the substrate.

② Since undissolved powder lumps tend to be formed when dissolving the water-soluble polymer in the water for thickening, dissolving takes a long time.

③ The water-soluble polymer elutes from the obtained electrode by contacting the electrolyte (strong alkali solution) and may eventually cover the entire surface of the active material, thus diminishing its activity. With further elution of the water-soluble polymer, the active material will fall off to adversely affect battery characteristics.

An object of the present invention is to provide a thickener without liability of forming undissolved lumps in adding water for thickening, capable of thickening in a short time, enabling the uniform application without the sedimentation of the active material or the conductive agent even when the adding amount is small, having good applicability without stringiness nor sagging after application, and further providing an electrode not liable to elute to electrolyte; and to provide a composition for preparing an electrode paste for alkaline storage batteries using the thickener and the electrode paste. That is, thickeners of the present invention for electrode pastes for alkaline storage batteries comprise water-insoluble water-absorbent resins.

Further, an electrode paste composition for alkaline storage battery of the present invention comprises an active material, a conductive agent, a fluorine resin and a thickener, wherein the thickener is a water-insoluble water-absorbent resin.

Furthermore, an electrode paste for alkaline storage battery of the present invention comprises an active material, a conductive agent, a fluorine resin, a thickener and water, wherein the thickener comprises a water-insoluble water-absorbent resin.

Water-insoluble water-absorbent resins used in the present invention are not particularly limited as long as the resin swells by water absorption and is insoluble in water. Those having a carboxylic acid salt group are preferable, such as (1) water-insoluble water-absorbent resins obtained by polymerizing a vinyl monomer having a carboxylic acid group, a copolymerizable crosslinking agent and optionally starch and/or another vinyl monomer, followed by neutralizing with an alkaline compound to effect at least partial neutralization of carboxylic acid groups, (2) water-insoluble water-absorbent resins obtained by polymerizing a vinyl monomer having a carboxylic acid salt group alone or a carboxylic acid group and a carboxylic acid salt group, a copolymerizable crosslinking agent and optionally starch and/or another vinyl monomer, (3) water-absorbent water-insoluble resins obtained by polymerizing a vinyl monomer which forms a carboxylic acid salt group by hydrolysis, and optionally a copolymerizable crosslinking agent and another vinyl monomer, followed by hydrolyzing with an alkaline compound to have a partially carboxylic acid salt group, and (4) water-insoluble water-absorbent resins obtained by crosslinking a water-soluble polymer having a carboxylic acid salt group after polymerization.

Examples of such vinyl monomers having a carboxylic acid group include unsaturated mono- or poly- carborylic acid such as (meth)acrylic acid, crotonic acid, sorbic acid, maleic acid, itaconic acid and cinnamic acid, and anhydrides thereof such as maleic anhydride. "(Meth)acrylic ..." herein denotes "acrylic ..." and/or "methacrylic ...".

Examples of vinyl monomers having a carboxylic acid salt group include alkali metal salts (such as salts of sodium, potassium or lithium), alkaline earth metal salts (such as salts of calcium or magnesium), ammonium salts or amine salts (such as salts of alkyl amines including methyl amine and trimethyl amine; salts of alkanol amines including triethanol amine and diethanol amine) of the above mentioned vinyl monomers having a carboxylic acid group, or a combination of two or more. Among these examples, sodium salts or potassium salts are preferable.

Examples of vinyl monomers which may acquire a carboxylic acid salt group by hydrolysis include methyl (meth)acrylate, ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, vinyl acetate and (meth)acrylonitrile.

Examples of copolymerizable crosslinking agents include ① compounds having at least two polymerized double bonds and ② compounds having at least one polymerizable double bond and at least one group reactive with a carboxylic acid salt group.

Examples of ① compounds include N,N'-methylene bis(meth)acrylamide; di- or tri- (meth)acrylate of polyols such as ethylene glycol, trimethylol propane, glycerol, polyoxyethylene glycol and polyoxypropylene glycol; divinyl benzene, divinyl toluene, tetraallyloxyethane and diallyl adipate.

Examples of ② compounds include ethylenically unsaturated compounds having a group reactive with a carboxyl group such as a hydroxyl group, an epoxy group, an amino group and a quaternary ammonium salt group. Suitable unsaturated compounds having a hydroxyl group include N-methylol (meth)acrylamide; suitable unsaturated compounds having an epoxy group include glycidyl (meth)acrylate; and suitable unsaturated compounds having a quaternary ammonium salt group include (meth)acryloyl oxyethyl trimethyl ammonium chloride and chlorides of trimethyl aminopropyl (meth)acrylamide.

Among these copolymerizable crosslinking agents, the ① compounds are preferable, in particular N,N'-methylene bisacrylamide, ethylene glycol diacrylate, trimethylol propane triacrylate and tetraallyloxy ethane. Examples of other vinyl monomers include hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, (meth)acrylamide, vinyl acetate and vinyl pyrrolidone.

Examples of alkaline compounds include hydroxides of alkali metals (such as sodium hydroxide, potassium hydroxide and lithium hydroxide), carbonates of alkali metals (such as sodium carbonate and sodium bicarbonate), amine compounds, ammonium compounds and combinations of two or more of the above. Among these examples, sodium hydroxide, potassium hydroxide and sodium bicarbonate are preferable.

Concrete examples of the water-insoluble water-absorbent resins include partially neutralized crosslinked graft copolymers of starch-acrylic acid, partially neutralized crosslinked polyacrylic acid, saponified copolymers of acrylate-vinyl acetate, partially neutralized crosslinked copolymers of isobutylene-maleic anhydride, alkaline metal salts of crosslinked carboxymethyl cellulose and partially neutralized self-crosslinked polyacrylic acid salts.

The ratio of monomers having a carboxylic acid salt group to total monomers constituting the water-insoluble water-absorbent resin in the present invention is, generally 40 mole % or more, preferably 50 to 80 mole %. It is preferable to have the percentage content of 40 % or more since the viscosity of the water-insoluble water-absorbent resin obtained will not deteriorate, providing good operativity in production.

The weight ratio of copolymerizable crosslinking agent based to the sum of the monomers which constitute the water-insoluble water-absorbent resin is, generally 0.01 to 10 %, preferably 0.1 to 5 %. It is preferable that the ratio be 0.01 % or more to ensure that the gel strength at the time of water absorption will not lower, nor form a sol, consequently not providing stringiness. It is further preferable since it provides dispersion stability of active material. Further, it is preferable that the ratio be 10 weight % or less to ensure that the gel strength will not become so great as to diminish its property of increasing the viscosity of the paste.

The weight ratio of vinyl monomers excluding the above mentioned vinyl monomers, namely the above mentioned "other vinyl monomers" based to the total monomers which constitute the water-insoluble water-absorbent resin is, generally 30 % or less, preferably 10 % or less.

By further crosslinking with a compound having at least two groups reactive with a functional group of the water-insoluble water-absorbent resin, a water-insoluble water-absorbent resin having a higher gel strength and property for increasing the viscosity and dispersion stability of an active material can be produced.

Examples of such compounds include compounds having at least two groups reactive with a carboxylic acid salt group, such as an epoxy group, a hydroxyl group, an isocyanate group and a quaternary ammonium salt group, and polyvalent metal compounds capable of forming an ion crosslinking.

Examples of such compounds include polyepoxy or polyglycidyl ether compounds such as ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, glycerol-1,3-diglycidyl ether, polyethylene glycol diglycidyl ether and bisphenol A-epichlorohydrin type epoxy resins; polyols such as glycerol, ethylene glycol and propylene glycol; and (poly)alkylene polyamines such as ethylene diamine.

Examples of polyvalent metal compounds include compounds capable of forming an ion crosslinking, for instance alkaline earth metals such as calcium and magnesium, hydroxides of zinc, aluminum or titanium, halogen compounds

of the above mentioned metals, and salts of the above mentioned metals such as sulfates, carbonates and acetates. Specifically, calcium hydroxide, zinc acetate and aluminum sulfate are included.

Among these examples, polyglycidyl ether compounds and polyvalent metal compounds are preferable.

The form of the water-insoluble water-absorbent resins of the present invention is not particularly limited, and any shapes such as powdery, flake, spherical and fibrous can be used. Fine powders having an average particle size of 200 μm or smaller are preferable. Fine powders having an average particle size of 100 μm or smaller are more preferable. It is preferable to use fine powders having an average particle size of 200 μm or smaller since the swelled particles of the resin after absorption of water will not become too large, with a preferable viscosity of the paste facilitating application onto a porous metal substrate.

The viscosity of the water-insoluble water-absorbent resins of the present invention is not particularly limited, but it is preferablly 20,000 cps or more when determined for an aqueous dispersion of water-insoluble water-absorbent resin with 1 weight % concentration at 30 °C. It is preferably 20,000 cps or more, since an active material having a large specific gravity can then be uniformly maintained in a dispersed state. Further, it is preferable that the upper limit of the above mentioned viscosity of water-insoluble water-absorbent resins is 100,000 cps or less, to facilitate preparation and adjustment of the paste.

The thickeners of the present invention may include further thickeners, if required. Examples of such further thickeners include water-soluble polymers such as carboxy methyl cellulose (CMC), polyvinyl alcohol and sodium polyacrylate. Their percentage content based on total thickeners is 30 weight % or less.

Thickeners of the present invention can be used for any electrode paste for alkaline storage batteries, for which water-soluble polymers have been used conventionally. In particular, among alkaline storage batteries, thickeners of the present invention are preferably used for a nickel-cadmium battery or a nickel-hydrogen battery.

The process of forming an electrode by using a thickener of the present invention is not particularly limited as long as a thickener of the present invention is used in place of a conventional water-soluble polymer. That is, an aqueous solution of a water-soluble polymer is to be replaced by an aqueous dispersion of a water-insoluble water-absorbent resin of the present invention. However, the amount of a thickener of the present invention can be less than that of a water-soluble polymer. Specifically, the amount of a thickener of the present invention based on the water content in the paste is, generally 0.1 to 2.0 weight %, preferably 0.2 to 1.0 weight %. The viscosity of the paste including materials such as an active material and a conductive agent is, generally 10,000 to 40,000 cps. By having 0.1 weight % or more of a water-insoluble water-absorbent resin, sedimentation of an active material in the paste is prevented to facilitate the uniform application to a metal porous substrate. Further, sagging of the paste after application to the metal porous substrate is also prevented. It is also preferable to have 2.0 weight % or less of a water-insoluble water-absorbent resin, since fluidity of the paste is preferably maintained to facilitate the applicability to the metal porous substrate.

It is preferable to have high percentage of an active material in the paste of the present invention with respect to battery performance. However, if too much is present, the applicability and adhesion to the metal porous substrate is diminished. Generally, the amount is 200 to 300 weight parts to 100 weight parts of an aqueous dispersion of a thickener.

A porous metal substrate, which is a part of an electrode material of an alkaline storage battery, is not particularly critical in construction and conventional materials employed for the purpose can be used. Examples of porous metal substrates include porous metal substrates with two-dimentional structure such as a metal net of nickel as the main component; and metal substrates produced by forming holes in a metal plate of nickel as the main component by punching (They are generally called "punched metal"); porous metal substrates with three-dimentional structure such as a formed metal, including those prepared by plating a polyurethan foam with nickel, followed by burning and eliminating the polyurethane component leaving a porous structure of nickel; and metal fiber nets such as those prepared by applying nickel-plating on a net formed from fibers.

To make an electrode, compositions for preparing electrode paste for an alkaline storage battery according to the present invention are mixed with water to form a paste and then applied to metal porous substrates such as described above, dried and pressure-molded. The temperature of the drying is not particularly limited, but is in general 100 to 200 °C.

A composition for preparing an electrode paste for an alkaline storage battery contains an active material, a conductive agent, a fluorine resin and a thickener. In particular, it is characteristic of the present invention that a water-insoluble water-absorbent resin is used as a thickener. Thickeners contribute to thickening a paste for an electrode and to affixing an active material and a conductive agent to a metal porous substrate after drying and solidification of the paste. However, they also contribute to a diminishing of the electric characteristics of the battery: therefore, to that extent, it is desirable to limit the less amount of thickener. Since water-insoluble water-absorbent resins are used as a thickener in the present invention, a reduced amount can be sufficient to provide the effects compared with the case where water-soluble resins ar used as a thickener.

The proportions of active material, conductive agent, fluorine resin and thickener are generally, based on 100 weight parts of an active material; 0.05 to 7 weight parts, preferably 0.1 to 5 weight parts, of a conductive agent; 0.2 to 10 weight parts, preferably 0.5 to 7 weight parts, of a fluorine resin; and 0.01 to 2 weight parts, preferably 0.05 to 1

weight part of a thickener. In order to make a paste, a further 1 to 200 weight parts, preferably 5 to 100 weight parts, of water is added thereto. Then the paste is applied to the above mentioned metal porous substrates as a paste of the present invention.

Different kinds of active materials are used depending on whether a positive electrode or negative electrode is concerned. Examples of active materials for the positive electrode include nickel hydroxide powders. Examples of active materials for the negative electrode include cadmium powders and hydrogen-storing alloy powders. Hydrogen-storing alloys reversibly store hydrogen in an alkaline electrolyte by an electro-chemical reaction and are well known as an active material for the negative electrode for an alkaline storage battery. Examples of hydrogen-storing alloys include $LmNi_{4.2}Co_{0.2}Mn_{0.3}Al_{0.3}$ (Lm herein denotes La enriched misch metal.), $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$, $La_{0.8}Nd_{0.15}Zr_{0.03}Ni_{3.8}Co_{0.7}Al_{0.5}$, $MmNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.3}$ (Mm herein denotes misch metal), $MmNi_{2.5}Co_{0.7}Al_{0.8}$, $Mm_{0.85}Zr_{0.15}Ni_{1.0}Al_{0.8}V_{0.2}$, $ZrV_{0.41}Ni_{1.6}$, $ZrMn_{0.6}Cr_{0.2}Ni_{1.2}$, TiNi-$Ti_2Ni$ and TiNi-Zr_1Ni_{10}. Misch metal comprises a mixture of rare earth metals such as La, Ce and Nd.

Examples of conductive agents include materials used as conductive agents for an electrode paste, such as carbon black powders, nickel powders and cobalt powders.

Fluorine resins are used as a binder to firmly affix an active material. Examples of fluorine resins include polytetrafluoroethylene, tetrafluoroethylene-hexafluoropropylene copolymers, and a combination of these fluorine resins and thermoplastic resins such as polyvinyl alcohol, styrene-butadiene copolymers and styrene-isopropylene copolymers.

The present invention will be further explained with reference to Examples hereinafter, but the invention is not limited to these embodiments. "Part" and "%" in Examples and Comparative Examples denote "weight part" and "weight %", respectively. Viscosity of a water-insoluble water-absorbent resin or a water-soluble polymer was measured in the method described below.

Viscosity measuring method : A uniform water-absorbent gel is prepared by adding 1 part of a water-insoluble water-absorbent resin or a water-soluble polymer to 99 parts of deionized water. Viscosity is measured with a B-type viscometer (6 rpm) with the temperature of the gel maintained at 30 °C.

Example 1

34 parts of sodium acrylate, 28 parts of acrylic acid, 0.5 part of N,N'-methylene bisacrylamide and 400 parts of water were placed in an openable sealed container. After adjusting the liquid temperature to 20 °C in nitrogen atmosphere, 1 part of an aqueous solution of ammonium persulfate having 0.5 % concentration and 1 part of an aqueous solution of sodium hydrogensulfite having 0.5 % concentration were added for polymerization to form a gel with heat generation. After six hours from starting the polymerization, the obtained crosslinked gel polymer containing water was taken out. The crosslinked gel polymer was cut finely by kneading for approximately two hours with a kneader, and drawn on a drum drier which was pre-heated to 160 °C to dry, then pulverized to obtain a water-insoluble water-absorbent resin (A) having an average particle size of 35 μm. The viscosity of the water-insoluble water-absorbent resin (A) obtained was 31,000 cps, and it was a thickener of the present invention.

Example 2

Example 1 was repeated except that the 0.5 part of N,N'-methylene bisacrylamide was replaced with 0.8 part of trimethylolpropane triacrylate. A water-insoluble water-absorbent resin (B) was obtained. The average particle size of the water-insoluble water-absorbent resin (B) was 35 μm and the viscosity thereof was 38,000 cps, and it was a thickener of the present invention.

Example 3

100 parts of acrylic acid, 0.5 part of tetra allyloxyethane and 400 parts of water were placed in an openable sealed container. After adjusting the liquid temperature to 10 °C in nitrogen atmosphere, 1 part of an aqueous solution of hydrogen peroxide having 1 % concentration and 1 part of an aqueous solution of ascorbic acid having 0.5 % concentration were added for polymerization to form a gel with heat generation. After six hours from starting the polymerization the sealed container was opened to take out the obtained crosslinked gel polymer containing water. After cutting 500 parts of the gel finely, 73.5 parts of an aqueous solution of sodium hydroxide having 50 % concentration was added thereto for neutralization, then further kneaded uniformly to convert approximately 75 mole % of polyacrylic acid in the polymer to sodium polyacrylate. The neutralized gel was dried with a drum drier which was pre-heated to 160 °C, then pulverized to obtain a water-insoluble water-absorbent resin (C) having an average particle siz of 35 μm. The viscosity of the obtained water-insoluble water-absorbent resin (C) was 55,000 cps, and it was a thickener of the present invention.

Example 4

The neutralized gel of Example 3 was pulverized immediately after neutralizing to obtain a water-insoluble water-absorbent resin (D) having an average particle size of 250 µm. The viscosity of the obtained water-insoluble water-absorbent resin (D) was 57,000 cps, and it was a thickener of the present invention.

Example 5

After adding 300 parts of water to 100 parts of the water-insoluble water-absorbent resin obtained in Example 2 to uniformly absorb water, 2 parts of glycerol was added and uniformly kneaded. The water-absorbent gel was dried with hot air at 160 °C, and pulverized to obtain a water-insoluble water-absorbent resin (E) having the average particle size of 35 µm. The viscosity of the obtained water-insoluble water-absorbent resin (E) was 16,000 cps, and it was a thickener of the present invention.

Comparative Example 1

A water-soluble polymer, CMC (carboxymethyl cellulose) commercially available as "CMC DAICEL 1160" (Tradename) produced by DAICEL CHEMICAL INDUSTRIES, LTD. was used as a thickener (F). The average particle size thereof was 200 µm or less, and the viscosity was 500 cps.

Comparative Example 2

A mixture of CMC (carboxymethyl cellulose) "CMC DAICEL 1160" (Tradename) and sodium polyacrylate commercially available as "ARONBIS-S" produced by NIHON JUNYAKU, CO., LTD. in the weight ratio of 5 to 1 was used as a thickener (G). The average particle size thereof was 200 µm or less, and the viscosity was 450 cps.

Example and Comparative Example concerning electrode paste

Thickeners of the present invention, namely, the water-insoluble water-absorbent resins (A), (B), (C), (D) and (E) obtained in Examples 1 to 5 and thickeners obtained in Comparative Examples 1 and 2 were evaluated by making electrode pastes. Evaluation was conducted by the following procedure : 250 parts of hydrogen-storing alloy powders (200 mesh pass) of $LmNi_{4.2}Co_{0.2}Mn_{0.3}Al_{0.3}$ (Lm denotes La enriched misch metal.), a thickener in a predetermined amount, 3.8 parts of polytetrafluoroethylene (PTFE), 2.5 parts of carbon black and 100 parts of water were kneaded and mixed to adjust the paste. The kinds and amounts of thickeners are described in Table 1.

Each paste was applied to the both side surfaces of a punched-metal substrate having 1 mm thickness and 2.0 mm hole diameter with 50 % rate of hole area, by soaking the substrate in a paste placed in a container, lifting vertically, then passing through a slit to remove surplus paste. Then the substrate was dried at 150 °C for 20 minutes followed by rolling with a roller press.

Efficiency of thickening (in preparing a paste), sagging of paste, and ease of applicability of a paste were examined. Further, fallout property of the active material after soaking the substrate in 35 % aqueous solution of potassium hydroxide and leaving at 60 °C for one week was also examined.

(Evaluation standard)

① Efficiency of thickening (in preparing a paste)
  ○ : Undissolved powder lumps are seldom formed and the paste thickens uniformly in a short time.
  X : Undissolved powder lumps are often formed and a long time is needed for uniform thickening.
② Sagging of a paste
  ○ : Paste does not sag when left in the vertical position after applying to the substrate.
  △ : Paste sags a little when left in the vertical position after applying to the substrate.
  X : Paste sags when left in the vertical position after applying to the substrate.
③ Applicability of a paste
  ○ : Paste can be applied to a predetermined thickness after passing through the slit.
  △ : Paste can with difficulty be applied to a predetermined thickness after passing through the slit.
  X : Paste can not be applied to a predetermined thickness after passing through the slit.
④ Fallout property of an active material after application
  ○ : Active material does not fall out.
  △ : Active material falls out a little.
  X : Active material falls out considerably.

Table 1

	Kind of thickener	Amount (part) of thickener	efficiency of thickening	sagging of paste	applicatility of paste	fallout property after application
1	A	0.50	O	O	O	O
2	B	0.50	O	O	O	O
3	C	0.50	O	O	O	O
4	D	0.50	O	O	Δ	Δ
5	E	0.50	O	Δ	O	O
6	F	0.50	X	X	X	X
7	F	2.00	X	Δ	Δ	Δ
8	G	2.00	X	Δ	Δ	Δ

From the evaluation results reported in Table 1, it can be seen that an electrode for an alkaline storage battery produced with a thickener of the present invention is superior to conventional water-soluble polymers since it has better efficiency of thickening, is not liable to sag even with a little amount of adding, and has better applicability of paste without liability of fallout of active material.

By using a thickener of the present invention in production of an electrode paste for an alkaline storage battery, the following advantageous effects can be achieved.

(1) In the thickening stage, undissolved powder lumps are seldom formed and the paste can be gelled uniformly in a short time.
(2) Thickening effect can be realized by adding an amount less than that of conventional water-soluble polymers to prevent sagging of the paste.
(3) Owing to the absence of stringiness, good operativity in application to a porous metal substrate can be provided.
(4) Since thickener does not elute from the obtained electrode even after contacting with elecrolyte (strong alkaline solution) and the entire surface of an active material can hardly be covered with a thickener, the activity of the active material can be maintained for a long time and fallout of active material seldom occurs.

Since thickeners of the present invention have the advantageous effects heretofore mentioned, they can be applied preferably in production of paste used for a positive electrode such as a nickel positive electrode, or a negative electrode such as a cadmium negative electrode and a hydrogen-storing alloy negative electrode of alkaline storage batteries such as nickel-cadmium batteries and nickel-hydrogen batteries. Since paste for an alkaline storage battery including the thickener has the above mentioned advantageous effects, it is useful as a paste for electrode of an alkaline storage battery.

Claims

1. A thickener for electrode paste for an alkaline storage battery, comprising a water-insoluble water-absorbent resin.

2. The thickener according to claim 1, wherein the water-insoluble water-absorbent resin has carboxylic acid salt groups and a viscosity, determined on an aqueous dispersion of 1 weight % concentration at 30 °C, of at least 20,000 cps.

3. The thickener according to claim 1 or 2, wherein the water-insoluble water-absorbent resin is in the form of a powder having an average particle size of 200 μm or less.

4. A composition for an electrode paste for an alkaline storage battery, comprising an active material, a conductive agent, fluorine resin and a thickener, wherein the thickener comprises a water-insoluble water-absorbent resin.

5. The composition according to claim 4, wherein the water-insoluble water-absorbent resin has carboxylic acid salt groups and a viscosity, determined on an aqueous dispersion of 1 weight % concentration at 30 °C, of at least 20,000 cps.

6. The composition according to claim 4 or 5, wherein the water-insoluble water-absorbent resin is in the form of a powder having an average particle size of 200 µm or less.

7. The composition according to any one of claims 4 to 6, wherein the proportions of conductive agent, fluorine resin and thickener, based on 100 parts of an active material, are : 0.05 to 7 weight parts of conductive agent, 0.2 to 10 weight parts of fluorine resin and 0.01 to 2 weight parts of thickener.

8. An electrode paste for an alkaline storage battery comprising an active material, a conductive agent, a fluorine resin, a thickener and water, wherein the thickener comprises a water-insoluble water-absorbent resin.

9. The electrode paste according to claim 8, wherein the water-insoluble water-absorbent resin has carboxylic acid salt groups, and a viscosity, determined on an aqueous dispersion of 1 weight % concentration at 30 °C, of at least 20,000 cps.

10. The electrode paste according to claim 8 or 9, wherein the proportions of conductive agent, fluorine resin, thickener and water, based on 100 parts of an active material, are: 0.05 to 7 weight parts of conductive agent, 0.2 to 10 weight parts of fluorine resin, 0.01 to 2 weight parts of thickener and 1 to 200 weight parts of water.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 0013

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y	US-A-5 212 622 (MACFARLANE DOUGLAS R ET AL) 18 May 1993 * column 2, line 61 - column 3, line 32 * * examples 1-3 * * claims 1-35 * ---	1 2-10	H01M4/62 H01M4/24 C08L1/26 C08L3/04
X Y	DATABASE WPI Section Ch, Week 8304 Derwent Publications Ltd., London, GB; Class A85, AN 83-08594K & JP-A-57 202 658 (MATSUSHITA ELEC IND KK) , 11 December 1982 * abstract * ---	1 2-10	
Y	EP-A-0 284 063 (TOKYO SHIBAURA ELECTRIC CO ;TOSHIBA BATTERY (JP)) 28 September 1988 * page 4, line 4-9 * * examples 1-5 * ---	4-10	
Y	EP-A-0 574 019 (FURUKAWA BATTERY CO LTD) 15 December 1993 * page 3, line 15-35 * * page 9, line 6-31 * * example 1 * ---	4-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01M C08L
X Y A	DATABASE WPI Section Ch, Week 9506 Derwent Publications Ltd., London, GB; Class A18, AN 95-041419 & JP-A-06 322 178 (SANYO CHEM IND LTD) , 22 November 1994 * abstract * --- -/--	1 2,3 4-10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	28 March 1996	Engl, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
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EUROPEAN SEARCH REPORT

Application Number
EP 96 10 0813

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 9520 Derwent Publications Ltd., London, GB; Class A14, AN 95-149660 & JP-A-07 053 884 (MITSUBISHI PETROCHEMICAL CO LTD) , 28 February 1995 * abstract *	1	
Y		2,3	
A		4-10	
X	DATABASE WPI Section Ch, Week 8951 Derwent Publications Ltd., London, GB; Class A85, AN 89-373896 & JP-A-01 279 562 (SHARP KK) , 9 November 1989 * abstract *	1	
Y		2,3	
A		4-10	
A	PATENT ABSTRACTS OF JAPAN vol. 011 no. 027 (E-474) ,27 January 1987 & JP-A-61 198561 (HITACHI MAXELL LTD) 2 September 1986, * abstract *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	28 March 1996	Engl, H

CATEGORY OF CITED DOCUMENTS

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